P1242 /WOD
Search report

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,037,144

1,037,144

Date of Application and filing Complete Specification Dec. 7, 1964.
No. 49623/64.
Application made in United States of America (No. 334721) on Dec. 31, 1963.
Complete Specification Published July 27, 1966.

Index at acceptance: —C3 P(2A, 2D1A, 2P6H, 2P6X, 7A, 7D1A, 7D1C, 7D2A1, 7D2A2B, 7D3, 7P6H, 7P6X); C3 R(27K4F, 27K5F)

Int. Cl.: —C 08 f 1/22//C 08 g

COMPLETE SPECIFICATION

Method and Apparatus for Forming a Polymer Film

We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of Armonk New York 10504, United States of America (assignees of RICHARD ALLEN CONNELL and LAWRENCE VINCENT GREGOR), do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method and apparatus for forming a polymer film on a substrate.

It is well known that various chemical reactions may be initiated by means of an energy discharge. For example, polymerization reactions may be conducted by energy discharge is an atmosphere containing a monomer vapour. Energy discharge has also been employed in chemical plasma reactors for the synthesis of various compounds. Related procedures involve the use of electron beams to polymerize organic vapours which are absorbed on substrates thereby forming insulating films.

The source of the energy discharge used in such processes is ordinarily an electric arc struck between two electrodes so as to form a plasma with the organic vapours. The plasma thus formed cannot be precisely defined but it is generally believed to comprise a mixture of electrons and gaseous monomer ions, free radicals and various charged molecular fragments, with or without neutral atoms. This plasma is then ordinarily directed onto a suitable substrate. The substrate conventionally is an electrically charged element which attracts the electrons and ions in the plasma. It is thought that excited organic constituents of the plasma are then deposited and subsequently polymerize on the surface of the target forming thin insulating films. It is also common practice to direct the plasma through a template, screen or mask to control the areas of the substrate on which the polymer film is deposited.

In the course of operating conventional systems of the type described, certain problems have been encountered which render the various techniques somewhat unsatisfactory.

According to known discharge polymerization methods, a relatively large energy input and a high pressure must be maintained in order to produce satisfactory discharge and plasma production. As a result, a considerable amount of polymer deposition occurs at random on the walls of the reaction chamber and elsewhere other than on the substrate.

Also, as a result of the high energy input and pressure, the entire system including the substrate frequently is heated to a temperature at which degradation or pyrolysis of the monomer or polymer occur. As a consequence the films deposited by such techniques have not been uniform in their chemical or physical properties. Nor has the polymer film had the composition that would be expected from the polymerization of the monomer vapour.

Where arcing of electrodes in the atmosphere containing a monomer vapour has been used as the energy source for plasma formation, undesirable spattering, sputtering and local arcing have been experienced.

A major use of the polymer films of the type in question has been in the production of dielectric layers in thin film capacitors. The electrodes of such devices are frequently formed by vacuum deposition of the electrode metal directly onto the dielectric layer. It is highly desirable, therefore, to have compatible methods for depositing dielectric and electrode films so that the methods can be operated alternately with ease and efficiency, and pre-

ferably in an integrated system, to build up a multi-layer device.

However, if high monomer pressures are required, as they are in conventional plasma polymerization systems, a great deal of pumping is required to prepare the chamber for a subsequent vacuum, deposition.

Also, in the plasma deposition devices currently in use, the substrate or target is ordinarily an electrode in the system. This too may result in overheating of the substrate and adversely affect the homogeneous character and properties of the polymer film.

Where masks or templates are interposed between the plasma source and the substrate, a problem referred to as "shadowing" has also been encountered. Shadowing refers to the deposition of the polymer film on areas of the substrate intended to be screened or masked by the template. This results from diffusion of monomer ions within the space between the template and the substrate and the deposition of polymer film on portions of the substrate where film formation is not desired and is found in most conventional processes.

According to the present invention there is provided a method of forming a polymer film on a substrate by producing in the presence of the substrate a plasma resulting from a glow discharge in a vapour of one or more ethylenically unsaturated monomers, wherein the glow discharge is produced by subjecting the vapour simultaneously to a radio-frequency electric field and to a magnetic field.

Preferably a second magnetic field aiding the first magnetic field is applied to the plasma at a position such as to propel the plasma towards the substrate.

The present invention also provides apparatus for forming a polymer film on a substrate, comprising a chamber, a support for supporting the substrate within the chamber, a device for introducing a vapour of one or more ethylenically unsaturated monomers into the chamber, a source arranged to apply a radio-frequency electric field to monomer vapour introduced by the said device into the chamber and means arranged to apply a magnetic field simultaneously with the electric field to monomer vapour introduced by the said device into the chamber, the magnetic and electric fields being such as to effect a glow discharge resulting in a plasma.

The methods and apparatus of the present invention have wide utility in the coating arts and are especially useful in depositing thin insulating polymer films of uniform thickness and accurately determined dimensions. Such methods may be employed in the production of thin film electrical devices, such as capacitors where the thin metal films or plates may be deposited by gas plating techniques.

Although the mechanism of formation of the polymer film is open to speculation, the methods and apparatus of the present invention may be utilized to form polymer films from a wide variety of monomers and mixtures of monomers, including, for example, styrene, divinylbenzene, butadiene, epoxy monomers e.g. glycidyl methacrylate and allyl glycidyl ether, and alkylenes, such as ethylene and propylene.

The invention will now be described by way of example with reference to the accompanying drawings in which:—

Figure 1 is a partially schematic, cross-sectional view of apparatus in accordance with the invention for performing the method according to the invention,

Figure 2 is a graph of the rate of deposition of polystyrene when deposited in accordance with the method of the invention, and,

Figure 3 is a graph of the rate of deposition of polydivinylbenzene when deposited in accordance with the method of the invention.

Referring to Fig. 1, in a reaction chamber 10 is mounted a substrate 11 and mask 12 which together are referred to as the target.

An inlet 15 is provided at one end of the reaction chamber for admitting a monomer vapour into the chamber. The admission of the monomer vapour through inlet 15 is preferably controlled by a needle valve 16. A thermocouple gauge 17 may be provided adjacent to the gas inlet in order to monitor the pressure at the inlet. Valve 16 communicates with a suitable source of monomer vapour 18.

A portion of reaction chamber 10 is surrounded by a radio-frequency coil 20 which may be energized by any conventional variable radio-frequency source, not shown.

A second coil 21 surrounds a major portion of the reaction chamber 10 including most of the region from the radio-frequency coil 20 to the substrate 11. Coil 21 is connected to a suitable source of direct current, not shown.

In operation of the system, needle valve 16 is actuated so as to admit a monomer vapour to maintain a controlled low pressure within the system.

Coils 20 and 21 are both energized and the combination of the radio-frequency energy input and the magnetic field produces a controlled, sustained glow discharge in chamber 10. The dc magnetic field generated by coil 21 also has the affect of confining the plasma in a region axial to coils 21 and 20 and generally perpendicular to the surface of substrate 11.

The confining effect of the magnetic field produced by coil 21 reduces the random deposition on the walls of the chamber to an extent less than would otherwise be the case and enhances deposition on the surface of substrate 11.

It is supposed that the collimating or confining effect of the magnetic field increases

the number of useful collisions between particles in the plasma and thereby enables the glow discharge to be sustained with a low energy input to the radio-frequency coil 20.

The system may be connected t a vacuum pump, not shown, through outlet 30 to maintain a slight pressure gradient within the system. This also assists the diffusion of the plasma in the direction of the substrate.

Substrate 11 is preferably mounted on a water cooled metal block 13. Block 13 is pivoted on shaft 14 so that the substrate may be caused to face a port 40 through which it may be exposed to a vacuum deposition operation after the polymer deposition is completed. Block 13 may be of copper or another metal having good thermal conductivity and may be cooled by the internal circulation of water or other cooling fluid. Similarly, coils 20 and 21 may be cooled by water.

In one embodiment of the invention, a pinch coil 22 may be provided surrounding the reaction chamber. Pinch coil 22 is connected with a suitable source of direct current, not shown, to provide a secondary, local magnetic field which preferably is positioned on the side of the plasma formation zone remote from the substrate.

The magnetic field produced by coil 22 reinforces locally the magnetic field generated by coil 21 so that the combined magnetic field effect is greater in the region of coil 22 than elsewhere along the axis of coil 21. This produces a pinching or squeezing effect on the plasma generated in the chamber and tends to propel the plasma towards substrate 11.

In order to deposit polymer films with this apparatus, a monomer vapour is admitted from source 18 by manipulation of valve 16 to produce at the inlet end of chamber 10 a low pressure of up to 200 microns, depending on the monomer being used. A thermocouple gauge 17 or other means for measuring the pressure at the inlet system may be used, so that the amount of monomer admitted through valve 16 may be maintained at a desired level.

While the precise temperature of the system is not critical a temperature in the reaction chamber in the range of from 0° C to 30° C is satisfactory for most polymer depositions.

The chamber is pumped out through line 30 so that the pressure at the outlet end of the chamber is within the approximate range of 10 to 20 microns. The evacuation thus maintains a slight pressure gradient in the chamber which also tends to assist the diffusion of the plasma towards the target. This pressure gradient maintains a flow rate of a few cubic centimetres per second of monomer vapour through the plasma formation zone.

When desired pressure has been established in chamber 10 as indicated by thermocouple gauge 17, a glow discharge is initiated by energizing coil 20 with radio-frequency energy and by passing direct current through coil 21.

The electromagnet energy from the radio-frequency coil 21 and the magnetic field of coil 21 are sufficient to trigger the glow discharge at a relatively low energy input.

It is important to note that the dc magnetic field of coil 21 also tends to collimate or confine the plasma particles along the axis of the coil which is perpendicular to the surface of the substrate. The magnetic field also extends close to the surface of the substrate, so that control of the diffusion of the plasma particles is obtained throughout the major part of the chamber.

Coil 20 is connected to a suitable source of radio-frequency electric energy operable at frequencies of from 100 kilocycles to 1 megacycle per second, so as to generate a peak field of about 2 oersteds.

The solenoid 21 may be connected to any suitable dc power supply and is operated to generate peak magnetic fields of up to 1000 oersteds. Higher magnetic field strengths may be used, but there is a practical limit to the strength of magnetic fields that can be generated by a solenoid, such as coil 21, without undue heating. Even at field strengths of from 400 to 500 oersteds, it is desirable to provide cooling means for the solenoid coil.

In general, a magnetic field strength of 300 oersteds or greater is sufficient to enable the glow discharge to be triggered.

It is also possible to employ permanent magnets in place of solenoids 21 and 22 to provide the required magnetic field.

Where a pinch coil 22 is employed, it is also connected to a suitable source of dc current. The solenoid may be operated to generate a magnetic field of several hundred oersteds.

The invention will be more fully understood with reference to the following detailed examples in which the reference numerals refer to parts of the apparatus of Fig. 1.

Example 1

Monomeric styrene vapour is introduced from source 18 through valve 16 into chamber 10. The temperature in the chamber is maintained at about 25° C and a pressure of about 160 microns is established at the inlet end of chamber 10. Radio-frequency coil 20 is then energized and is operated at a frequency of about 400 kilocycles per second to generate a peak field of about 2 oersteds. A current of 0.4 amps and 10 volts in coil 20 will provide about 4 watts of radio-frequency power in the chamber adjacent to the coil. Solenoid 21 is simultaneously energized and is operated to generate a magnetic field of about 500 oersteds.

The combined electromagnetic input from coils 20 and 21 triggers and sustains a glow

discharge which is visible in chamber 10. The plasma then diffuses into contact with substrate 11, which is an evaporated metal film, in the chamber 10 resulting in the deposition of a thin polystyrene film on the substrate.

Referring to Figure 2 of the drawing, it will be seen that extremely high rates of polystyrene film deposition are obtained by this method. Of course, films of any desired thickness may be built up by controlling the length of time that the substrate is exposed to the plasma.

EXAMPLE 2

Divinylbenzene monomer vapour is introduced into chamber 10 which includes a substrate 11 of an evaporated metal film. The vapour is introduced to produce pressure of about 50 microns at the inlet end of chamber 10. Radio-frequency coil 20 is energised to generate a peak field of about 1 oersted. Solenoid 21 is operated to provide a field strength of about 300 oersteds. The energisation of the coils 20 and 21 sustains a glow discharge visible in the chamber 10. The temperature of the system is maintained at 25° C by cooling copper block 13 and by cooling coils 20 and 21.

The rate of deposition of polydivinylbenzene, as conducted according to Example 2, is shown in Figure 3 of the drawing.

EXAMPLE 3

Polymer deposition is carried out as in Example 2, but an additional collimating or pinch coil 22 is operated during the deposition to provide a secondary magnetic field having a field strength of about 150 oersteds.

It will be apparent from the foregoing examples that other monomers may be converted to plasma and deposited as polymeric films by proceeding in a similar manner.

In general, a pressure of up to 200 microns and preferably 20 to 200 microns is satisfactory in the present process. With a pressure in the indicated range, a magnetic field strength of about 300 oersteds or greater in combination with an energy input from a radio-frequency coil which is operated at a frequency of from 100 kilocycles to 1 megacycle per second and which has a peak field strength of up to 2 oersteds will trigger and sustain a satisfactory glow discharge.

Due to the low temperatures which are maintained and the absence of local arcing, no spattering, sputtering is experienced. Also, the collimating effect of the magnetic field minimizes random deposition of polymer on the walls of the chamber, concentrates the deposition on the substrate and reduces "shadowing".

The use of the magnetic field to confine the plasma also results in high efficiency in terms of film growth rate for the power expended. As seen in Figure 2, film growth rates of 1600 Å per minute have been achieved with very little substrate heating or shadowing of the polymer films.

The present controlled glow discharge for plasma formation and deposition may be used to deposite thin, uniform insulating films for thin film capacitors, the plates of which are evaporated metal films. Insulating films as thin as 100 Å may also be produced from a number of different organic monomers. The magnetically focused glow discharge also permits greater control of the nature of the polymer film, yields a much more homogeneous film and especially permits control of the thickness and dimensions of the deposited film.

WHAT WE CLAIM IS:—

1. A method of forming a polymer film on a substrate by producing in the presence of the substrate a plasma resulting from a glow discharge in a vapour of one or more ethylenically unsaturated monomers, wherein the glow discharge is produced by subjecting the vapour simultaneously to a radio-frequency electric field and to a magnetic field.

2. A method according to claim 1, wherein the electric field has a peak strength substantially equal to 2 oersteds and the magnetic field has a strength of at least 300 oersteds.

3. A method according to claim 1 or 2, wherein a second magnetic field aiding the first magnetic field is applied to the plasma at a position such that the plasma is propelled towards the substrate.

4. A method according to any one of the preceding claims wherein the monomer vapour consists of a mixture of different monomers.

5. Apparatus for forming a polymer film on a substrate comprising a chamber, a support for supporting the substrate within the chamber, a device for introducing a vapour of one or more ethylenically unsaturated monomers into the chamber, a source arranged to apply a radio-frequency electric field to monomer vapour introduced by the said device into the chamber and means arranged to apply a magnetic field simultaneously with the electric field to monomer vapour introduced by the said device into the chamber, the magnetic and electric fields being such as to effect a glow discharge resulting in a plasma.

6. Apparatus according to claim 5, wherein the radio-frequency source is arranged to apply an electric field having a peak strength substantially equal to 2 oersteds and the means for applying a magnetic field is arranged to apply a magnetic field having a strength of at least 300 oersteds.

7. Apparatus according to claim 5 or 6, wherein further means are provided for applying a second magnetic field to a plasma produced within the chamber, the second magnetic field aiding the first and being such as

to propel the plasma to a substrate supported by the support.

8. Apparatus according to claim 7, wherein the chamber comprises a tubular portion having an inlet at one end for monomer vapour and the support is arranged to support a substrate at the other end, the radio-frequency source including a coil surrounding the tubular portion of the chamber and the means for applying the first mentioned magnetic field and the second magnetic field including respectively second and third coils surrounding the said tubular portion, the second coil being substantially co-extensive with the said tubular portion and the third coil extending over a region of the tubular portion at the inlet end.

9. A method of forming a polymer film by producing in the presence of a substrate, a plasma resulting from a glow discharge in a vapour of one or more ethylenically unsaturated monomers, the method being substantially as hereinbefore described with reference to any one of the Examples.

10. Apparatus for forming a polymer film by producing in the presence of a substrate a plasma resulting from a glow discharge in a vapour of one or more ethylenically unsaturated monomers, the apparatus being substantially as hereinbefore described with reference to and as shown in Fig. 1 of the accompanying drawings.

For the Applicants:
F. N. BLAKEMORE,
Registered Patent Agent.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

This drawing is a reproduction of the Original on a reduced scale.

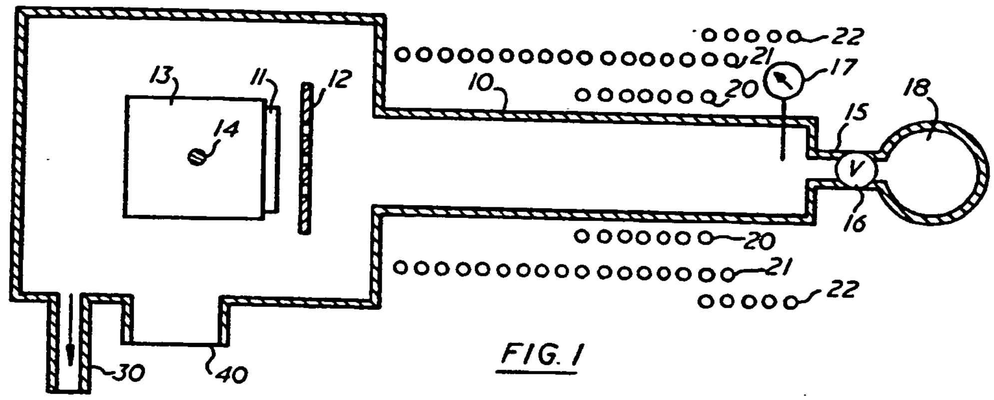

FIG. 1

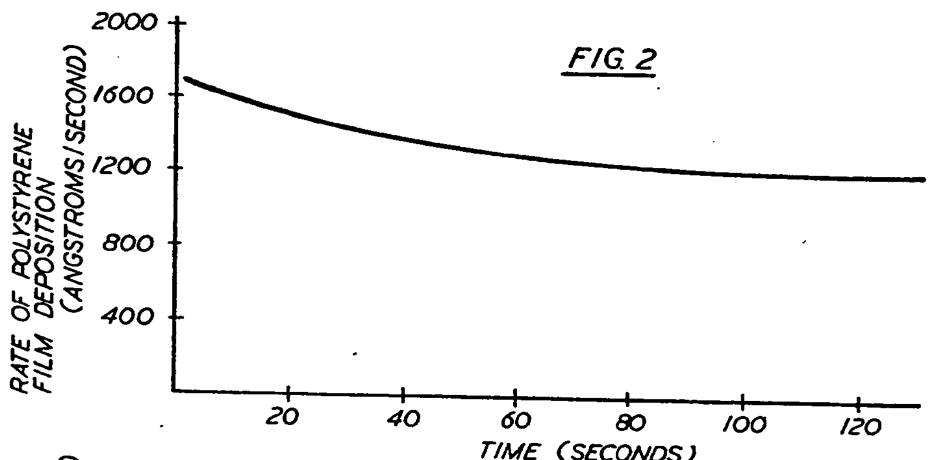

FIG. 2

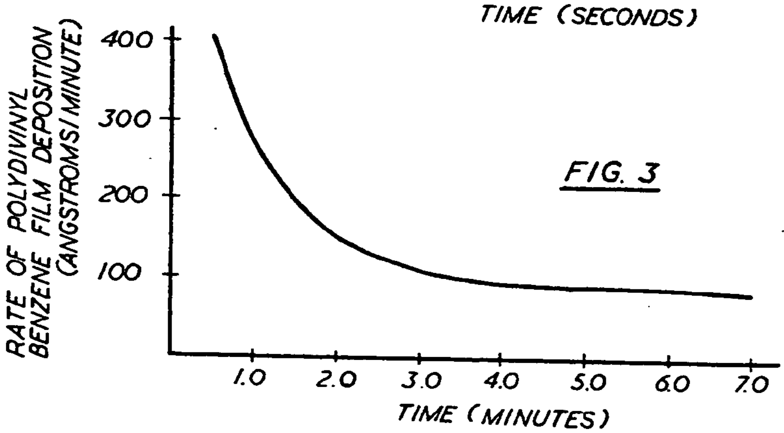

FIG. 3